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(54) A process for the treatment of  
polyacetal articles

(57) To improve the adhesion of a metallized coating applied to a polyacetal article by a sputtering technique, the article is surface treated, prior to metallization, by an acidic solution. The acidic solution may be composed of an aqueous solution of one or more inorganic acids and/or one or more organic acids and/or one or more acidic oxidizing mixtures. After surface treatment and before metallizing, the article may be treated with an agent for neutralizing the acidic solution.

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## SPECIFICATION

## A process for the treatment of polyacetal articles

- 5 This invention relates to a process for the treatment of polyacetal articles prior to metallization thereof by a cathode sputtering technique, and also relates to a process of metallizing polyacetal articles. 5

Generally, the metallization by means of sputtering, which is applied to plastics (e.g. ABS articles is effected in order to impart a metallic lustre thereto. One such conventional process 10 comprises degreasing the article with the appropriate solvent, coating and the article with an undercoat of a paint (such as a urethane, an acrylic urethane or an acrylic ester), drying the undercoat, sputtering chromium (SUS-304), a chromium alloy, of aluminium in an argon atmosphere at a pressure of  $5 \times 10^{-3}$  to  $2 \times 10^{-4}$  Torr so as to form a metal layer with a thickness of 300 to 1,000 Å, and then applying a top coat (such as an acrylic ester or acrylic urethane) to the metallized article. 15

However, in the case of polyacetal articles, there is currently no material for the undercoat which has good enough adhesion to the object to be of practical use, because polyacetal is highly crystalline and chemically stable. Thus, the above-described conventional process cannot be used for metallizing polyacetal articles. It has now been found that the surface treatment of 20 polyacetal articles using an acidic solution is very effective promoting strong adhesion of an undercoat to the articles. Additionally such a surface modification does not deleteriously affect the surface smoothness, further provides a good surface suitable for sputtering metals. Suitable inorganic acids include hydrochloric acid, sulphuric acid, phosphoric acid and mixtures thereof, and an oxidizing mixture consisting of potassium dichromate and sulphuric acid. Suitable 25 organic acids include acetic acid and p-toluene sulphonic acid. A mixed acid consisting of an inorganic acid and an organic acid may be used in this invention. Although the treatment condition varies with the type of acid being used, favourable effects can be expected particularly when one or a mixture of inorganic acids are employed with high concentration. 25

In the case of organic acid solutions, the treatment temperature may be 0 to 100°C, whilst 30 the treatment time is preferably not more than 360 minutes. 30

In the case of inorganic acid solutions and oxidizing mixtures, the treatment temperature may be 0 to 80°C whilst the treatment time is preferably not more than 30 minutes.

More specifically, in the case of acid mixtures, for example, when the acid solution is composed of 30–60 percent by weight of sulphuric acid, 5–30 percent by weight of 35 hydrochloric acid, and 65–10 percent by weight of water, the preferred temperature is between 0 and 30°C and the preferred time is not greater than 15 minutes. In one preferred embodiment, the acid solution consists of 20–50 percent by weight of sulphuric acid, 30–50 percent by weight of phosphoric acid, and 50–0 percent by weight of water. In the case of an oxidizing mixture, one preferred mixture consists of 1–5 percent by weight of potassium 40 dichromate, 50–95 percent by weight of sulphuric acid, and 49–0 percent by weight of water. 40

After surface modification of the polyacetal article, the article is dipped into a neutralizing solution to neutralize any acidic material on the surface of the article and then an undercoat is applied. Subsequently, drying of the undercoat is carried out (for example at 120°C for 30 minutes) and then the metallization by sputtering is performed. Thus, a metal layer with uniform 45 thickness is formed on the undercoat without giving any micro-cracks. 45

The term "polyacetal" as used herein includes any grade of polyacetal homopolymers, polyacetal copolymers having different compositions, and polyacetal homopolymers or copolymers modified with various kinds of compounds.

Examples of the modifiers include fillers (e.g.  $\text{CaCO}_3$  or talc), inorganic reinforcing agents (e.g. 50 glass fibres, beads, glass flakes or mica), organic reinforcing agents, organic modifiers, and stabilizers of any kind. 50

The present invention will be explained more in detail according to the following examples.

Plates of DURACON M90 (a polyacetal resin produced by Polyplastics Co., Ltd.) having a length of 70mm, a width of 50mm, and a thickness of 3mm, were solvent degreased using an 55 organic solvent (e.g. isopropylalcohol or acetone) and were then surface treated under a variety of conditions as shown in the Table. Any adherent acid coating on the plates was then neutralized by immersing the plates in a neutralizer (e.g. a 50 % by weight sodium hydroxide aqueous solution). After that, EXP 1245 (an urethane paint, a sputtering undercoat for ABS resin manufactured by Fujikura Kasei Co., Ltd.) was applied to the surface-treated plates and 60 dried at 120°C for 30 minutes. 60

These undercoated plates were placed in a sputtering apparatus sold as CFS-8ES manufactured by Tokuda Manufacturing Co. Ltd., and then a chromium alloy was sputtered on it so as to produce a 300–400 Å thick chromium surface layer.

EXP 1380 (an acrylic urethane paint, a topcoat made by Fujikura Kasei Co., Ltd.) was painted 65 onto the metallized plates which were then dried at 80°C for 30 minutes to complete curing of 65

the topcoat.

If desired or necessary, before acid treatment, the polyacetal articles may be subjected to an annealing step by heat treatment, for example, at 140°C for 1 hour, for stress relieving purposes.

- 5 In order to compare the degree of the adhesion of each deposit (undercoat + sputtered metal layer + topcoat) to the substrate of Duracon, a cellophane adhesive tape, which was applied to the deposit in which 1 mm × 1 mm checkers had been produced by two mutually perpendicular sets of parallel cuts through the deposit, was peeled off at an angle of 180° to the surface to which the adhesive tape was adhered. The number of checkers left behind on the substrate was  
10 counted. The lustre of the sputtered metal layers on the sample were visually compared. The results are shown in the Table. 10

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N.B. \*1)  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4/\text{H}_2\text{O} = 40/40/20$  (wt %)  
 \*2)  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O} = 5/80/15$  (wt %)  
 \*3)  $\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O} = 35/8/57$  (wt %)

Table 1

Example	Agents used for treatment	Treatment condition	Peeling-off resistance (left-behind checkers/ total checkers)	Luster
Example 1	88% $\text{H}_2\text{SO}_4$	25°C X 30 sec.	100/100	Good
2	98% $\text{H}_2\text{SO}_4$	25°C X 180 sec.		
3	50% $\text{H}_2\text{SO}_4$ solution	25°C X 5 min.		
4	50% $\text{H}_2\text{SO}_4$ solution	25°C X 30 min.		
5	85% $\text{H}_3\text{PO}_4$ solution	25°C X 10 min.		
6	85% $\text{H}_3\text{PO}_4$ solution	25°C X 30 min.		
7	20% HCl solution	25°C X 10 min.		
8	20% HCl solution	25°C X 30 min.		
*1) 9	$\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4/\text{H}_2\text{O}$	25°C X 5 min.		
*1) 10	$\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4/\text{H}_2\text{O}$	25°C X 30 min.		
*2) 11	$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$	25°C X 20 sec.		
*2) 12	$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$	25°C X 180 sec.		
*3) 13	$\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O}$	25°C X 3 min.		
*3) 14	$\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O}$	25°C X 15 min.		
15	10% p-toluene sulphonic acid solution	80°C X 10 min.		
16	10% p-toluene sulphonic acid solution	80°C X 30 min.		
17	80% glacial acetic acid solution	25°C X 60 min.		
18	80% glacial acetic acid solution	25°C X 180 min.		
19	10% $\text{H}_2\text{SO}_4$ solution	80°C X 5 min.		
20	10% $\text{H}_2\text{SO}_4$ solution	80°C X 20 min.		
21	(30% $\text{H}_2\text{SO}_4$ + 5% p-toluene sulphonic acid) solution	30°C X 20 min.		
22	(30% $\text{H}_2\text{SO}_4$ + 5% p-toluene sulphonic acid) solution	30°C X 40 min.		
Comp. Example 1	Untreated	—	0/100	Good
2	Sandpapered	—	100/100	Bad

## CLAIMS

1. A process for the treatment of a polyacetal article prior to metallizing by sputtering, which process comprises surface treating the article with an acid solution.
2. A process as claimed in claim 1, in which the acidic solution is an aqueous solution of one or more inorganic acids. 5
3. A process as claimed in claim 1, in which the acidic solution is an aqueous solution of one or more organic acids.
4. A process as claimed in claim 1, in which the acidic solution is an aqueous solution of one or more inorganic acids, and one or more organic acids.
- 10 5. A process as claimed in claim 1, in which the acid solution is an oxidizing mixture of one or more salts, one or more inorganic acids, and water. 10
6. A process as claimed in claim 1, substantially as hereinbefore described in any one of Examples 1 to 22.
7. A polyacetal article whose surface has been treated, prior to metallizing by sputtering, by 15 a process as claimed in any preceding claim. 15
8. A process of producing a metallized polyacetal article comprising surface treating a polyacetal article by a process as claimed in any one of claims 1 to 6 and subsequently metallizing said treated article by a sputtering technique.
9. A process as claimed in claim 8, wherein after surface treatment and before metalliza- 20 tion, the article is treated with an agent for neutralizing the acidic solution. 20
10. A polyacetal article when metallized by a process as claimed in claim 8 or 9.

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